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Identification of Volatile Hydrocarbons as Mobile Source Tracers for Fine-Particulate Organics

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16. ABSTRACT

Several volatile organic compounds (VOCs) have been identified as candidates for tracers of fine particulate carbon and EOM from mobile sources. The identification resulted from a multiple screening procedure in which the ambient concentrations of a candidate VOC were first required to have both a high correlation with ambient concentrations of fine particulate Pb, a well established tracer of mobile source emissions, and a low correlation with soil-corrected fine particle potassium (K'), a previously demonstrated tracer of woodsmoke, using measurements from an airshed in which these were the dominant sources. Each VOC surviving this screening was then substituted in place of Pb, and along with K', in multi-linear regression representations of the carbon and EOM data. Successful VOCs resulted in a multiple correlation coefficient (r^2) at least as good as with K' and Pb, and estimates of the woodsmoke and mobile source contributions virtually the same as with K' and Pb. The reasonableness of these VOCs as mobile source tracers was affirmed by considering what is known about the abundance of those VOCs in woodsmoke and mobile source emissions.

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Identification of Volatile Hydrocarbons as Mobile Source Tracers for Fine-Particulate Organics

PB90-245697

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■ Several volatile organic compounds (VOCs) have been identified as candidates for tracers of fine-particulate carbon and extractable organic matter (EOM) from mobile sources. They include *o*-xylene, 2-methylhexane, 3-methylhexane, methylcyclohexane, 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, and 2-methylpentane. The identification resulted from a multiple-screening procedure in which the ambient concentrations of a candidate VOC were first required to have both a high correlation with ambient concentrations of fine-particulate Pb, a well-established tracer of mobile source emissions, and a low correlation with concentrations of soil-corrected fine-particle potassium (K′), a previously demonstrated tracer of wood combustion, using measurements from an airshed in which these were the dominant sources. Each VOC surviving this screening was then substituted in place of Pb, and along with K′, in multilinear regression representations of the carbon and EOM data. Successful VOCs resulted in a squared multiple-correlation coefficient (r^2) at least as good as with K′ and Pb and estimates of the wood combustion and mobile source contributions virtually the same as with K′ and Pb.

Introduction

Receptor-oriented modeling for source impact estimates uses primarily ambient physical/chemical measurements in the airshed of interest. Intrinsic to receptor modeling is that the basic information on which conclusions are based are the concentrations of chemical species as they actually exist in the atmosphere, implicitly including the complex influences of emissions rate, transport, deposition, and atmospheric chemistry. Thus, a compound that might appear a priori to be a good tracer on the basis of its abundance in a source's emissions may ultimately be unsatisfactory because of its other characteristics, such as deposition loss that is too different from the bulk of the source's emissions products or a loss due to atmospheric reactions. By focusing on the measured species at the point of interest in the ambient environment and their observed mutual correlations, much of the intervening complexity can be avoided.

Particulate lead (from the octane enhancer tetraethyllead) and bromine (from the lead scavenger ethylene dibromide) present in gasoline have traditionally been used as tracers for mobile sources. In July 1985, however, the amount of lead allowed in gasoline in the United States was reduced to 0.5 g/gal with a further reduction to 0.1 g/gal in January 1986 (*1*). In addition, most cars produced for sale in the United States since 1975 are equipped with catalytic converters and require unleaded gasoline. These events are causing mobile source related ambient concentrations of lead and bromine to diminish to the extent that either accurate measurements will no longer be possible or formerly negligible sources of ambient lead, e.g., incinerators and oil-fired power plants (*2*), will be competitive with motor vehicle derived lead. Recent wintertime receptor modeling studies (*3–5*) were successful in using fine-particle Pb, K, and ^{14}C as tracers for emissions from mobile sources and residential wood burning. However, finding suitable substitutes for lead as a mobile source tracer is critical for future receptor modeling activities.

During the winter of 1986, gaseous and particulate samples were collected in Boise, ID, as part of the Environmental Protection Agency's (EPA) Integrated Air Cancer Project (*6*). Boise has no major manufacturing or industrial sources and the airshed was mainly impacted by mobile sources and residential wood combustion. We report here the identification of a number of volatile hydrocarbons that were used to replace Pb in a multilinear regression receptor model (*3*) to calculate the contribution of mobile source emissions to the total carbon (C_t) and extractable organic matter (EOM) present in fine particles.

Experimental Methods

Between November 1986 and February 1987, samples were collected at two sites in Boise, ID. One site was located in a city park (Elm Grove Park) in the midst of a residential neighborhood impacted by wood combustion emissions from numerous single-family homes. The second site was on top of a fire station (fire station no. 5) adjacent to a major intersection. This site was expected to have a substantial impact from the emissions of motor vehicles.

Fine- (0–2.5-μm aerodynamic diameter) and coarse- (2.5–10-μm diameter) fraction particulate samples for inorganic analysis by X-ray fluorescence and [C_t] by combustion analysis (*7*) were collected on 37 mm diameter Teflon and quartz media, respectively, using dichotomous samplers. Fine-particulate samples for EOM were collected on Teflon-coated glass fiber filters, using both PM10 medium-flow samplers (0.113 m^3/min; 102 mm diameter filters) and standard Hi-vol samplers equipped with 2.5-μm impactors. Vapor-phase organic compounds (VOCs) were collected in evacuated 6-L stainless steel canisters. Consecutive 12-h dichotomous and Hi-vol samples (changeover at 7 a.m. and 7 p.m.) were collected throughout the entire week, but VOC and 102 mm filter particulate samples were collected during consecutive 12-h periods only from 7 a.m. Saturday through 7 a.m. Wednesday.

Hydrocarbon concentrations were determined by gas chromatography with flame ionization detection. Species in the C_2–C_5 molecular weight range were separated on a packed capillary (6.1 m × 1.6 mm) containing Durapak *n*-octane/Porasil C. Analysis of hydrocarbons in the C_5–C_{10} molecular weight range was performed on a 30-m DB-1 fused-silica column (0.25-μm coating). Identities were determined through retention time comparisons and mass spectral analysis. Hydrocarbon analyses in most cases involved a composite of two canister samples representing the same time period of either a weekend or weekday sampling period; e.g., Saturday and Sunday 7

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a.m.–7 p.m. were combined to make one weekend daytime sample. Typically, 0.5 L of each sample to be combined was cryogenically concentrated in the inlet system prior to injection.

Filters were Soxhlet extracted with dichloromethane, filtered (0.2 μm) and concentrated by rotary evaporation to 5 and 10 mL for the 102-mm and Hi-vol filters, respectively. The Hi-vol filters were individually extracted while the 102-mm filters were extracted in pairs, matching the sampling periods used for the VOC canister composites. The EOM was determined by duplicate gravimetric analyses of 0.250-mL aliquots of extract evaporated to dryness.

Receptor Modeling

Following the procedure described in ref 4, the source apportionment of C_t and EOM was performed with a single element tracer multiple linear regression (MLR) model of the form

$$Y_i = a(\text{woodsmoke tracer})_i + b(\text{mobile source tracer})_i + c \quad (1)$$

where Y = [EOM] or [C_t]. The subscripted quantities are measured simultaneously during each sampling period i, and the initially unknown coefficients a, b, and c are determined by MLR using data from all the sampling periods at both sites. Soil-corrected fine-particle potassium, K′, was used as a tracer for wood combustion:

$$[K'] = [K] - [Fe](K/Fe)_{soil} \quad (2)$$

where [K] and [Fe] are the fine-particle concentrations of potassium and iron from the sample and the average K/Fe ratio for soil was determined from the coarse dichotomous samples. The average correction for fine-particle potassium in Boise was 17%, i.e., [K] and [K′] averaged 135 and 112 ng/m^3, respectively. Lead or a VOC hydrocarbon was used as a mobile source tracer.

Results

In Boise, the average lead levels were 60 ng/m^3 or ~5 times lower than those observed for a similar study carried out just 2 years earlier in Albuquerque, NM (*4*). Apportionment of EOM and C_t for Boise was initially performed by MLR using corrected potassium and lead concentrations (*8*). The [C_t] regression was performed on >200 sampling periods from both sites, while the [EOM] regression was performed on data from 100 Hi-vol extracts. A chemometric procedure (*9*) was utilized to select 25 daytime and 25 nighttime filter samples from each site. Unfortunately, many of these initially selected 100 sampling periods did not include sampling periods for which VOC analyses were available. However, EOM data were available from the 102-mm filters, which were collected and extracted with the same pooling scheme as used for the VOC samples. Since the available VOC data represented the average of two separate 12-h sampling periods, subsets of data for C_t and EOM regression studies were prepared by averaging the individual potassium ([K′]), [Pb], and [C_t] values for the same composite VOC sample periods. The resulting C_t–VOC subset contained 84 cases while the EOM–VOC subset contained 71 cases for the two sites. The C_t–VOC subset contained additional cases because some VOC analyses were performed for individual 12-h sampling periods and could be matched up with 12-h C_t data.

Having obtained the two subsets for C_t and EOM, MLR was carried out for each using K′ and Pb to see if coefficients were similar to those for the larger data sets. The MLR equations were refined by plotting observed vs predicted values for C_t or EOM, which revealed apparent outliers. The resulting MLR equations for the subsets are given below along with those previously obtained for the entire data sets.

All C_t data:

$$[C_t] = (83 \pm 3)[K'] + (54 \pm 7)[Pb] + 1.5 \pm 0.4 \quad (3)$$

$$n = 226, r^2 = 0.85$$

C_t–VOC subset:

$$[C_t] = (81 \pm 6)[K'] + (51 \pm 15)[Pb] + 1.2 \pm 0.8 \quad (4)$$

$$n = 78, r^2 = 0.83$$

Initial EOM data (Hi-vol filters):

$$[EOM] = (117 \pm 8)[K'] + (66 \pm 16)[Pb] + 1.7 \pm 1.1 \quad (5)$$

$$n = 97, r^2 = 0.79$$

EOM–VOC subset (102-mm filters):

$$[EOM] = (117 \pm 9)[K'] + (59 \pm 22)[Pb] + 1.6 \pm 1.2 \quad (6)$$

$$n = 66, r^2 = 0.85$$

where the units of the measured quantities are micrograms per cubic meter throughout. The MLR equations for all data and the corresponding VOC subsets have nearly the same coefficients. The coefficient errors for the subsets are greater than those of the corresponding total data set, likely a reflection of the different number of cases, e.g., n = 226 vs 78. By insertion of measured averages for all the concentrations used in these equations, the average contributions of wood combustion and mobile sources are readily calculated to be 66 and 23%, respectively, of the average C_t concentration, and 70 and 21%, respectively, of the average EOM concentration. Additional unknown sources, as represented by the intercepts, comprise the remaining 9–11%. The mobile source contribution to C_t and EOM in the Boise winter airshed is seen to be quite modest, at least for the two sites at which ambient data were collected.

Correlations of [K′] and [Pb] with individual hydrocarbons were then calculated for each subset and are summarized in Table I. The ordering of the hydrocarbons in Table I is in descending order relative to the correlation with [Pb] observed for the C_t–VOC subset. The sequence of [Pb] correlations for the EOM–VOC subset is generally similar, but differs in detail. The high correlation of several hydrocarbons with [Pb], and equally important their low correlation with [K′], suggest they might serve as mobile source tracers in a simple airshed such as Boise in the winter. An additional 19 hydrocarbons were routinely measured but are not include in Table I as they were below the limit of detection in >30% of the samples. These compounds were mostly olefins and substituted benzenes.

Results for the apportionment of C_t and EOM by MLR using K′ with each VOC having desirable correlation characteristics as tracers are shown in Table II. Our choices for tracers include the xylenes, methylcyclohexane, 2- and 3-methylhexane, 2,3,4- and 2,2,4-trimethylpentane, and 2-methylpentane. Acetylene and toluene appear to be acceptable tracers for Boise, but may be less suitable in some situations (see below). Ethylene and benzene, which showed an increased correlation with [K′] and are not expected to be good tracers, are included for comparison. The regressions in Table II were performed with VOC species expressed as parts per billion carbon, ppbC, while [K′] was in units of micrograms per cubic meter.

Table I. Correlations of Hydrocarbons with [K′] and [Pb]

hydrocarbon	C_t—VOC subset (n = 78) [Pb] r^2	C_t—VOC subset (n = 78) [K′] r^2	EOM—VOC subset (n = 66) [Pb] r^2	EOM—VOC subset (n = 66) [K′] r^2	VOC[a] av ppbC
toluene[b]	0.889	0.206	0.872	0.215	29.9
2,3,4-trimethylpentane[b]	0.881	0.191	0.869	0.186	2.9
m- and *p*-xylene[b]	0.877	0.185	0.812	0.174	18.2
3-methylhexane	0.864	0.214	0.843	0.198	5.9
benzene	0.856	0.341	0.853	0.329	14.6
2,2,4-trimethylpentane[b]	0.854	0.127	0.813	0.109	7.0
o-xylene[b]	0.852	0.147	0.852	0.158	7.2
methylcyclohexane	0.851	0.200	0.857	0.189	3.0
2-methylpentane	0.846	0.170	0.852	0.164	11.6
2-methylhexane[b]	0.845	0.166	0.835	0.157	9.8
ethylbenzene[b]	0.821	0.188	0.793	0.218	4.2
acetylene	0.796	0.160	0.773	0.140	14.7
isopentane[c]	0.788	0.130	0.805	0.163	31.0
2,3-dimethylbutane	0.771	0.192	0.809	0.170	3.4
1-butene	0.751	0.279	0.561	0.213	1.7
n-pentane[b]	0.729	0.155	0.784	0.141	16.9
propene[b]	0.725	0.255	0.809	0.245	8.0
methylcyclopentane[b]	0.715	0.152	0.756	0.160	5.0
3-methylheptane	0.714	0.133	0.671	0.153	2.3
identified paraffins	0.692	0.172	0.705	0.171	227.7
2-methylheptane	0.682	0.107	0.664	0.121	1.8
2,4-dimethylpentane	0.672	0.192	0.664	0.178	3.0
n-octane	0.671	0.134	0.704	0.097	2.6
2-methyl-2-butene	0.612	0.143	0.651	0.151	2.9
3-methylpentane[b]	0.595	0.080	0.693	0.119	8.8
trans-2-pentene	0.576	0.112	0.559	0.093	1.8
cis-2-pentene	0.472	0.200	0.578	0.148	1.8
ethane	0.468	0.468	0.401	0.428	13.7
n-butane	0.463	0.049	0.499	0.031	43.7
n-hexane	0.423	0.063	0.355	0.049	13.3
propane	0.340	0.111	0.306	0.104	15.5
isobutane	0.294	0.037	0.273	0.022	12.8
ethylene	0.257	0.501	0.357	0.563	38.4
isoprene	0.239	0.055	0.159	0.007	1.4
dimethylcyclopentanes	0.200	0.176	0.169	0.199	4.1
n-heptane	0.095	0.043	0.104	0.039	7.2
2,3-dimethylhexane[b]	0.070	0.005	0.088	0.005	3.3
cyclohexane	0.009	0.066	0.031	0.115	4.9

[a] Average VOC concentration for the C_t—VOC subset. [b] Between one and three outlier data points deleted from regressions. [c] Interferences encountered in chromatography; n = 53 ([C_t]) and 47 ([EOM]).

Except for ethylene and benzene, the [K′] coefficients are all very close to those found with [Pb] (eqs 3–6). While the changes in the [K′] coefficients with ethylene and benzene may appear to be quite modest, the corresponding estimates for the mobile source contributions are affected much more. The estimates are ~50 and 34% higher for estimates based on the ethylene and benzene tracers, respectively, than the average estimate from the remaining VOCs in Table II. This is a result of the observation noted earlier that wood combustion, not mobile source emissions, is the dominant air pollution particulate contributor in this airshed.

Figure 1 is a plot of the predicted vs observed [EOM] obtained from the MLR of the EOM–VOC subset using K′ and Pb or K′ and 2,3,4-trimethylpentane, as a representative of the most promising VOC replacements for Pb. The fits are very similar.

Discussion

The identification of a VOC tracer for mobile source related particulate species should necessarily have the same origin, i.e., be a tailpipe emission. It should also be a minor emission of other sources in the airshed, i.e., wood combustion in the present study. The correlations in Table I are supported by the fact that the VOCs with the highest [Pb] correlations are predominantly associated with automobile tailpipe emissions as opposed to evaporative or refueling emissions. Figure 2 compares the distribution of hydrocarbon emission rates between tailpipe, evaporative, and refueling sources projected by EPA's Mobile4 model for several vehicle speed and ambient temperature combinations (*10*). At an average speed of 32 km h^{-1} (20 mi h^{-1}), evaporative emissions ranged from 34% of the total non-methane hydrocarbons (NMHC) at 10 °C (50 °F) to 73% at 38 °C (100 °F). The evaporative losses predicted here are for when the engine is not being operated, i.e., a parked car. The model returns a gram per kilometer value

Table II. Multilinear Regressions of [K′] and [VOC] vs [EOM] and [C_t]

hydrocarbon	[K′]	[VOC]	constant	r^2
Coefficients for MLR of Total Carbon, [C_t] (n = 78)				
acetylene	83.2 ± 5.7	0.17 ± 0.04	1.2 ± 0.8	0.81
2-methylpentane	84.4 ± 5.9	0.20 ± 0.06	1.4 ± 0.8	0.80
2-methylhexane	83.3 ± 5.8	0.27 ± 0.07	1.1 ± 0.8	0.81
3-methylhexane	81.7 ± 5.9	0.52 ± 0.13	0.9 ± 0.8	0.81
2,2,4-trimethylpentane	87.3 ± 5.9	0.23 ± 0.08	1.7 ± 0.8	0.80
methylcyclohexane	83.5 ± 6.0	0.73 ± 0.22	1.6 ± 0.8	0.80
2,3,4-trimethylpentane	83.2 ± 6.0	0.84 ± 0.24	1.3 ± 0.8	0.81
toluene	81.9 ± 5.9	0.09 ± 0.02	1.2 ± 0.8	0.81
m- and *p*-xylene	82.1 ± 5.8	0.16 ± 0.04	1.0 ± 0.8	0.82
o-xylene	83.2 ± 5.8	0.43 ± 0.12	0.8 ± 0.9	0.81
ethylene[a]	75.2 ± 7.6	0.09 ± 0.03	1.3 ± 0.8	0.80
benzene[a]	76.9 ± 6.4	0.24 ± 0.06	0.9 ± 0.8	0.82
Coefficients for MLR of Extractable Organic Matter, [EOM] (n = 66)				
acetylene	119 ± 8.1	0.20 ± 0.06	1.4 ± 1.2	0.83
2-methylpentane	118 ± 8.3	0.27 ± 0.09	1.3 ± 1.2	0.83
2-methylhexane	118 ± 8.2	0.32 ± 0.09	1.3 ± 1.2	0.83
3-methylhexane	116 ± 8.3	0.64 ± 0.19	0.9 ± 1.2	0.83
2,2,4-trimethylpentane	121 ± 8.3	0.34 ± 0.11	1.9 ± 1.1	0.83
methylcyclohexane	118 ± 8.5	0.94 ± 0.32	1.7 ± 1.2	0.82
2,3,4-trimethylpentane	116 ± 8.3	1.21 ± 0.33	1.1 ± 1.2	0.84
toluene	115 ± 8.6	0.12 ± 0.03	1.3 ± 1.2	0.83
m- and *p*-xylene	119 ± 8.4	0.16 ± 0.05	1.6 ± 1.2	0.83
o-xylene	118 ± 8.1	0.56 ± 0.16	0.6 ± 1.3	0.83
ethylene[a]	106 ± 11.7	0.11 ± 0.04	1.5 ± 1.2	0.82
benzene[a]	111 ± 9.0	0.29 ± 0.08	1.0 ± 1.2	0.83

[a] Compounds showing substantial correlation with [K′] and not expected to be good tracers; see Table I.

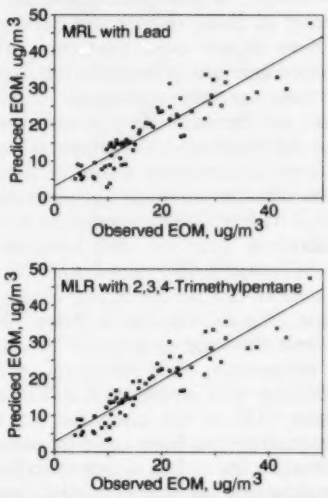

Figure 1. Plots of predicted vs observed ambient EOM concentrations from MLR calculations using K′ and lead or K′ and 2,3,4-trimethylpentane concentrations.

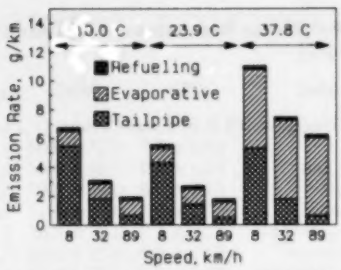

Figure 2. Distribution of mobile source related NMHC emissions as predicted by Mobile4 model.

for evaporative losses by assuming an average vehicle miles traveled (VMT) value. (Modeling of evaporative losses while vehicles are operating, running losses, is an area of current investigation by the EPA.) Evaporative and refueling emissions are dominated by butanes and pentanes, especially *n*-butane and isopentane (*11*, *12*). As seen in Table I, *n*-butane and isopentane were two of the most abundant VOCs yet had poor correlation with lead.

Tailpipe emissions are sensitive to the fuel, emission controls, driving cycles, etc. With the exception of the C_1–C_3 hydrocarbons and some olefins, much of the tailpipe emissions are a result of unburned fuel (*13*). Gasoline compositions vary widely with respect to individual hydrocarbons as refiners attempt to attain a specific octane rating and fuel vapor pressure. For example, the regular and premium gasolines used in a recent dynamometer study of in-use vehicle emissions (*12*) had 5 and 20 wt % toluene, respectively. Winter-grade gasolines, which would have been used in Boise during the current study, are blended to have higher vapor pressures, which usually include increased amounts of butanes and pentanes. Most detailed hydrocarbon data available on tailpipe emission rates, however, are limited to test procedures and studies carried out under relatively mild temperatures, i.e., 20–50 °C. Preliminary information suggests that during the winter months tailpipe emissions have increased fractions of unsaturated hydrocarbons, especially acetylene (*14*).

Ethane, ethylene, propene, and benzene had an increased correlation with [K′] relative to the other VOCs (Table I). Table III is a partial listing of results obtained from stack sampling at 10 homes in Boise. While all four compounds were observed as major VOC emissions, it is particularly noteworthy that ethylene, which has the highest correlation with ambient [K′] (Table I), was the most abundant VOC of the measured stack emissions. Acetylene frequently has been used by researchers as a means of estimating the mobile source contribution to total NMHC by multiplying the ratio of NMHC/acetylene from a tunnel or roadside mobile source sample times the [acetylene] in an ambient sample (*15*). While generally considered mainly a mobile source emission, stationary fuel combustion and waste burning and other fires have been reported to have acetylene emissions that are 5–8 wt % of the respective total source emissions (*15*). Table III also indicates residential wood combustion can be a significant source of acetylene. Although both the correlations (Table I) and MLR (Table II) indicate acetylene could serve as a tracer in the present study, it may not be applicable to other airsheds where burning or wood combustion are significant emissions. This may be particularly true in the future, as vehicular catalytic converter systems are quite efficient in the removal of acetylene resulting in decreased emissions relative to other tailpipe species (*16*).

In addition to acetylene, VOC signatures from sources have been used for source apportionment studies to estimate the contribution of sources to urban VOC levels (*17*–*19*). These studies used a source reconciliation or chemical mass balance approach employing an array of VOC source signatures. Mobile source signatures, however, may vary significantly from one vehicle to another, from one region to another, and with season. NMHC/acetylene ratios, for example, were found to be 26 in the Lincoln Tunnel in New York City in September 1982 (*16*), 17.7 in Raleigh, NC, in May 1983 (*20*), and 40 from laboratory dynamometer studies of vehicles after weighting model years to approximate the above Raleigh vehicle mix (*20*). These previous VOC receptor modeling studies did not address the apportionment of constituents of fine particles or consider the use of MLR modeling techniques to deduce the contribution of various emission sources to the total VOC concentrations.

Table III. Average Percent of Total NMHC Emissions

hydrocarbon	wood combustion[a]	tailpipe[b]
ethylene	13.91	8.72
ethane	9.40	2.48
benzene	6.99	3.77
acetylene	4.36	2.65
propene	4.16	2.99
toluene	3.78	6.56
1-butene	1.58	1.48
m- and *p*-xylene	1.39	3.10
o-xylene	0.57	2.09
3-methylhexane	0.51	1.23
2-methylpentane	0.38	1.72
2-methylhexane	0.33	1.71
methylcyclohexane	0.28	0.68
2,2,4-trimethylpentane	0.25	2.62
2,3,4-trimethylpentane	0.04	0.16

[a] From stack samples collected in Boise during IACP study. [b] Reference 12.

In the present work we have identified a number of volatile hydrocarbons that, at least in the Boise airshed, serve as satisfactory tracers to replace Pb in a MLR receptor model for estimating the contribution of mobile sources to the carbonaceous constituents of fine particles. Based on the screening criteria previously indicated, our choices include the xylenes, methylcyclohexane, 2- and 3-methylhexane, 2,3,4- and 2,2,4-trimethylpentane, and 2-methylpentane. In more complex airsheds, many of the VOCs that exhibited good correlations with lead in Boise may not be suitable. One possible VOC tracer candidate that was not measured in the current study is methyl *tert*-butyl ether (MTBE). This compound has recently been approved as an additive to gasoline (improves octane rating and helps in CO abatement) in amounts up to 15 wt %. While there is little information on its emission rates, its calculated atmospheric lifetime is about 5–25 days based on its rate of loss due to reactions with OH radicals. Particulate organic species, e.g., PAHs, nitroaromatics, and paraffins, in samples collected in Boise are currently being analyzed to determine which if any would serve as tracers for mobile sources and wood combustion.

Conclusions

This study has identified several VOCs as serious candidates for tracers of fine-particulate carbon and EOM from mobile sources. The identification resulted from a multiple-screening procedure in which the ambient concentrations of a candidate VOC were first required to have both a high correlation with ambient concentrations of fine-particulate Pb, a well-established tracer of mobile source emissions, and a low correlation with soil-corrected fine-particle potassium (K′), a previously demonstrated

tracer of woodsmoke, using measurements from an airshed in which these were the dominant sources. Each VOC surviving this screening was then substituted in place of Pb, and along with K′, in MLR representations of the carbon and EOM data. A successful VOC in this step was one that resulted in a squared multiple-correlation coefficient (r^2) at least as good as with K′ and Pb, and estimates of wood combustion and mobile source contributions virtually the same as with K′ and Pb. Finally, the reasonableness of the final VOCs as mobile source tracers was affirmed by considering what is known about the abundance of those VOCs in wood combustion and mobile source (both tailpipe and evaporative) emissions.

It remains to be seen whether these several VOCs will be useful as mobile source tracers in more complex airsheds and during different seasons. An encouraging feature of this study is that they seem to have worked well even though mobile source emissions was not the dominant source in the airshed.

Registry No. Toluene, 108-88-3; 2,3,4-trimethylpentane, 565-75-3; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 3-methylhexane, 589-34-4; benzene, 71-43-2; 2,2,4-trimethylpentane, 540-84-1; *o*-xylene, 95-47-6; methylcyclohexane, 108-87-2; 2-methylpentane, 107-83-5; 2-methylhexane, 591-76-4; ethylbenzene, 100-41-4; acetylene, 74-86-2; isopentane, 78-78-4; 2,3-dimethylbutane, 79-29-8; 1-butene, 106-98-9; *n*-pentane, 109-66-0; propene, 115-07-1; methylcyclopentane, 96-37-7; 3-methylheptane, 589-81-1; 2-methylheptane, 592-27-8; 2,4-dimethylpentane, 108-08-7; *n*-octane, 111-65-9; 2-methyl-2-butene, 513-35-9; 3-methylpentane, 96-14-0; *trans*-2-pentene, 646-04-8; *cis*-2-pentene, 627-20-3; ethane, 74-84-0; *n*-butane, 106-97-8; *n*-hexane, 110-54-3; propane, 74-98-6; isobutane, 75-28-5; ethylene, 74-85-1; isoprene, 78-79-5; dimethylcyclopentane, 28729-52-4; *n*-heptane, 142-82-5; 2,3-dimethylhexane, 584-94-1; cyclohexane, 110-82-7.

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